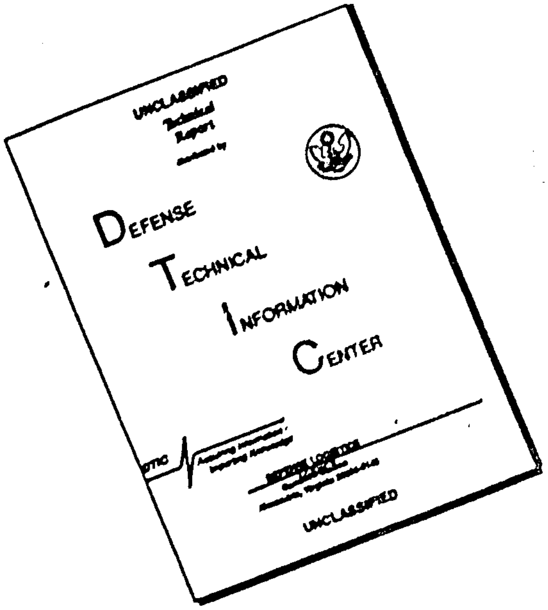
AD NUMBER
AD448226
LIMITATION CHANGES
TO: **Approved for public release; distribution is unlimited.**
FROM: **Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; 07 AUG 1964. Other requests shall be referred to Bureau of Naval Weapons, Washington, DC 20350.**
AUTHORITY
NAVAIR ltr dtd 26 Oct 1971

AD 448226

DISCLAIMER NOTICE



UNCLASSIFIED

DEFENSE TECHNICAL INFORMATION CENTER

UNCLASSIFIED

Linden Laboratories, Inc.
State College, Pennsylvania

First Quarterly Report

CHEMICAL STRENGTHENING OF CERAMIC MATERIALS

Prepared by: H. P. Kirchner
R. M. Gruver

7 August 1964

Prepared under Contract No. NOw 64-0381-C
for Bureau of Naval Weapons, Department of the Navy

Linden Laboratories, Inc.
State College, Pennsylvania

First Quarterly Report

CHEMICAL STRENGTHENING OF CERAMIC MATERIALS

7 August 1964

Prepared by: Henry P. Kirchner
Henry P. Kirchner
Project Director

Robert M Gruver
Robert M. Gruver
Technical Director

Prepared under Contract No. NOW 64-0381-C for the Bureau of Naval Weapons, Department of the Navy

NOTICES

QUALIFIED REQUESTERS MAY OBTAIN COPIES OF THIS REPORT DIRECT FROM THE DEFENSE DOCUMENTATION CENTER FOR SCIENTIFIC AND TECHNICAL INFORMATION. FOREIGN ANNOUNCEMENT AND DISSEMINATION OF THIS REPORT BY THE DEFENSE DOCUMENTATION CENTER IS LIMITED.

Only Department of Defense activities may reproduce this document in whole or in part without the express approval of the Chief of the Bureau of Naval Weapons.

Since this is a progress report, the information herein is tentative and subject to correction and modification.

FOREWORD

This quarterly report describes research performed on a program sponsored by the Bureau of Naval Weapons, Department of the Navy under Contract NOw-64-0381-C. This research was performed under the general technical direction of Mr. Charles F. Bersch, Code RRMA-34, of the Bureau of Naval Weapons.

This report covers work performed during the period 7 April 1964 to 7 July, 1964. The authors are pleased to acknowledge the contributions of many individuals, including especially Dr. W. R. Buessem and Mr. Ralph E. Walker, to this program.

ABSTRACT

An investigation of the effect of compressive surface layers on the strength of polycrystalline ceramic bodies is described. The compressive surface layers are formed by reactions in the surface of the material at high temperatures, which result in solid solutions having lower thermal expansion coefficients than the bulk of the material. Since the surface layers tend to contract less than the bulk of the material, they are placed in compression during cooling to room temperature.

The thermal expansion properties of a wide variety of oxide solid solutions were measured. Several of these materials have lower thermal expansion coefficients than the bodies on which they would be placed. Several methods of forming solid solution surface layers were investigated. Some of these methods show promise for formation of compressive surface layers.

TABLE OF CONTENTS

I. INTRODUCTION

Stronger ceramic materials are needed for radome and structural applications. Stronger materials can be helpful in reducing weight, and in improving rain erosion and thermal shock resistance.

This report describes an investigation of the strengthening effect of compressive surface layers on polycrystalline ceramic bodies. It is expected that the compressive stresses will reduce the contribution of surface flaws to the structural failure of these bodies.

Compressive surface layers can be formed in several ways. An extensive background for this work has been built up in the glass industry. Compressive layers on glasses have been achieved by overlaying one glass with another of different expansion coefficient, by quenching, by tempering, by ion exchange at relatively high temperatures to form a glass surface having a lower coefficient of thermal expansion than the bulk glass, by surface crystallization to form a lower expansion surface, and by exchange of larger ions for smaller ones at low temperatures resulting in "stuffing" the surface. Stronger polycrystalline materials resulting from various heat-treatments indicate the possible importance of residual stresses in determining the strength of these materials.

In the first part of this investigation, the compressive surface layers will be created by forming low-expansion surface layers at high temperatures. The low-expansion surface layers will be produced by chemical reactions which form solid solutions having lower coefficients of thermal expansion than the main body. In order to prevent the surface layers from shearing off, gradual composition variations will be used to form an expansion gradient which, in turn, will result in a stress gradient.

In the first quarter, effort was expended mainly in the search for new low-expansion solid solutions and in preliminary attempts to form low-expansion surface layers on polycrystalline ceramic bodies. In two systems, solid solution compositions were found that have lower expansion coefficients than the bodies on which they may be used. Preliminary thermal expansion measurements were made in several other solid solution systems. Some of the methods used for forming low-expansion surface layers show promise. This research is described in the following sections.

II. PROCEDURE AND RESULTS

A. Thermal Expansion of Oxide Solid Solutions

The literature on the thermal expansion of ceramics has been reviewed(1,2) and the thermal expansion of oxide solid solutions has been studied during recent programs(3-5). Solid solutions in the systems Al_2O_3-Cr_2O_3, TiO_2-SnO_2 and TiO_2-VO_2 have been investigated. The solutions in the system Al_2O_3-Cr_2O_3 have lower thermal expansion coefficients than Al_2O_3. The solutions in the system TiO_2-SnO_2 have lower expansion coefficients than TiO_2. The results of some of these measurements are given in Tables I and II.

Based upon these earlier results, measurements have been made on a number of other solid solution series. The objective of these measurements has been to add to the number of low-expansion solid solutions available for possible use as compressive surface layers. The following systems have been investigated:

MgO-NiO

MgO-ZnO

Al_2O_3-Cr_2O_3

Al_2O_3-Ga_2O_3

$MgO \cdot Al_2O_3$ (spinel) - Al_2O_3

TiO_2-SnO_2-VO_2

TABLE I

Thermal Expansion Data for Rutile Solid Solutions
(Room Temperature to 1000°C)

Mole % Additive	Linear Expansion Coefficient-/°C		Expansion Anisotropy -/°C	Volume Expansion Coefficient-/°C	Average Linear Expansion Coefficient-/°C
	α_{a_o}	α_{c_o}	$\alpha_{c_o}-\alpha_{a_o}=\Delta\alpha$	α_v	α_{av}
Pure TiO_2	83.4×10^{-7}	107.7×10^{-7}	24.3×10^{-7}	274.5×10^{-7}	91.5×10^{-7}
10 SnO_2	75.5	104.0	28.4	248.6	85.0
20 SnO_2	70.9	93.0	22.1	234.8	78.2
Pure SnO_2*	50.6	57.1	6.5	158.3	52.8

* 23-800°C

TABLE II

Thermal Expansion Data for Al_2O_3-Cr_2O_3 Solid Solutions
(400° to 1000°C)

Mole % Additive	Linear Expansion Coefficient (°C^{-1})x10^7		Expansion Anisotropy (°C^{-1})x10^7	Volume Expansion Coefficient (°C^{-1})x10^7	Average Linear Expansion Coefficient (°C^{-1})x10^7
	α_{a_o}	α_{c_o}	$\alpha_{c_o} - \alpha_{a_o} = \Delta\alpha$	α_v	α_{av}
Pure Al_2O_3	86.2	93.8	7.6	266.2	88.8
Al_2O_3+2.5 Cr_2O_3	87.4	95.1	7.7	269.9	89.8
Pure Cr_2O_3	78.2	72.9	-5.3	229.3	76.4
Cr_2O_3+10.0 Al_2O_3	78.0	72.5	-5.5	228.5	76.2

The various compositions in these systems were weighed and mixed by pressing through a 200 mesh screen. Binder was added and the discs were pressed and fired. The fired discs were broken up, ground in a Fisher automatic mortar and pestle and refired. In many cases the batches were ground and refired one or more times. Some of the details of these sample preparation procedures are given in Table III.

The equipment used for the X-ray thermal expansion measurements consisted of a General Electric XRD-5 diffractometer and a Tem-Pres high-temperature X-ray diffraction furnace. The sample holder is a platinum plate with a milled depression 13 by 16 by 0.75 mm deep. Because of the high thermal conductivity of platinum, the maximum difference in temperature across the specimen holder is 2° over the range 25° to 1000°C. A precision potentiometer is used to read the temperature during the diffraction peak measurement and the furnace is manually controlled. The specimen holder mounting is provided with rotational, tilting and translational adjustments so that the sample surface can be aligned on, and parallel to the diffractometer axis.

Copper radiation (λ=1.54050 Å for Kα_1) was used for all measurements. The X-ray tube was operated at 50 KV and 15 ma. with a 0.007-in. nickel filter. A 3° beam slit and a 0.2° detector slit were used with a scanning rate of 0.2° (2θ) per minute and a chart speed of 30 in. per hour. To attain precision and accuracy in the determination of lattice constants, use was made of lines in the back-reflection region.

TABLE III

Thermal Expansion Batch Compositions and Preparation and Procedures

Batch No.	Mole Fraction		Batch Wt. gms.	Firing Temp. °C	Firing Time	Refirings
1-1	1.0	MgO(1)	10	1500°C	1 hr.	1
1-2	0.8	MgO(1)	67.4			
	0.1	Ni_2O_3(2)	16.54	1500°C	1 hr.	1
1-3	0.6	MgO(1)	50.6			
	0.2	Ni_2O_3(2)	33.1	1500°C	1 hr.	1
2-1	1.0	Al_2O_3(2)	10	1500°C	1 hr.	1
2-3	0.8	Al_2O_3(3)	.814			
	0.2	Ga_2O_3(4)	.375	1500°C	1 hr.	1
3-2	0.9	Al_2O_3(9)	91.6	1500°C		
	0.1	Cr_2O_3(5)	15.2	2 times	1 hr.	1 overnight
3-3	0.8	Al_2O_3(3)	81.4	1500°C	1 hr.	1 overnight
	0.2	Cr_2O_3(5)	30.4	2 times		
Remake	0.7	Al_2O_3(10)	33.34	1000°C	1 hr.	
3-4	0.3	MgO(11)	4.032	1500°C 1300°C	overnight quench	
3-4	0.7	Al_2O_3(3)	91.6			
	0.3	Cr_2O_3(5)	15.2	1500°C	1 hr.	1
6-1	0.9	TiO_2(6)	44.94			
	0.1	VO_2(7)	2.765	1500°C	1 hr.	
6-2	0.8	TiO_2(6)	39.95			
	0.1	VO_2(7)	2.765	1500°C	1 hr.	
	0.1	SnO_2(8)	10.05			

TABLE III (Cont.)

(1) $MgCO_3$ Fisher Certified Reagent was used as source of MgO

(2) Baker Analyzed Reagent

(3) $Al(OH)_3$ Fisher Certified Reagent was used as source of Al_2O_3

(4) Ga_2O_3 was prepared at Linden Laboratories

(5) Fisher Certified Reagent

(6) TAMCO heavy grade TiO_2

(7) V_2O_5 Fisher Certified Reagent was used as source of VO_2

(8) Fisher Certified Reagent

(9) Norton Company Levigated Alumina was used as source of Al_2O_3

(10) Fisher Certified Reagent

(11) Ceramic Color & Chemical Co.

Thermal Expansion of Solid Solutions in the MgO-NiO System

The following solid solutions were prepared:

0.8 MgO-0.2 NiO
0.6 MgO-0.4 NiO
0.4 MgO-0.6 NiO

A fast scanning X-ray pattern indicated that the reaction was complete with formation of a single-phase material. The lattice spacings of the solid solutions are smaller than those of pure MgO.

The thermal expansion curves of these materials are shown in Figure 1 and the data are given in Table IV. The thermal expansions of the solid solutions are smaller than the thermal expansion of pure MgO. These reductions are smaller than expected and desired, but seem to be sufficient to justify further consideration of their possible usefulness for formation of compressive surface layers.

Thermal Expansion of Spinel Solid Solutions

The following solid solutions were prepared:

0.5 MgO-0.5 Al_2O_3
0.3 MgO-0.7 Al_2O_3
0.2 MgO-0.8 Al_2O_3

After firing overnight at 1500°C, the composition 0.5 MgO-0.5 Al_2O_3, the stoichiometric spinel composition, showed a major fraction of spinel and a minor fraction of periclase (MgO).

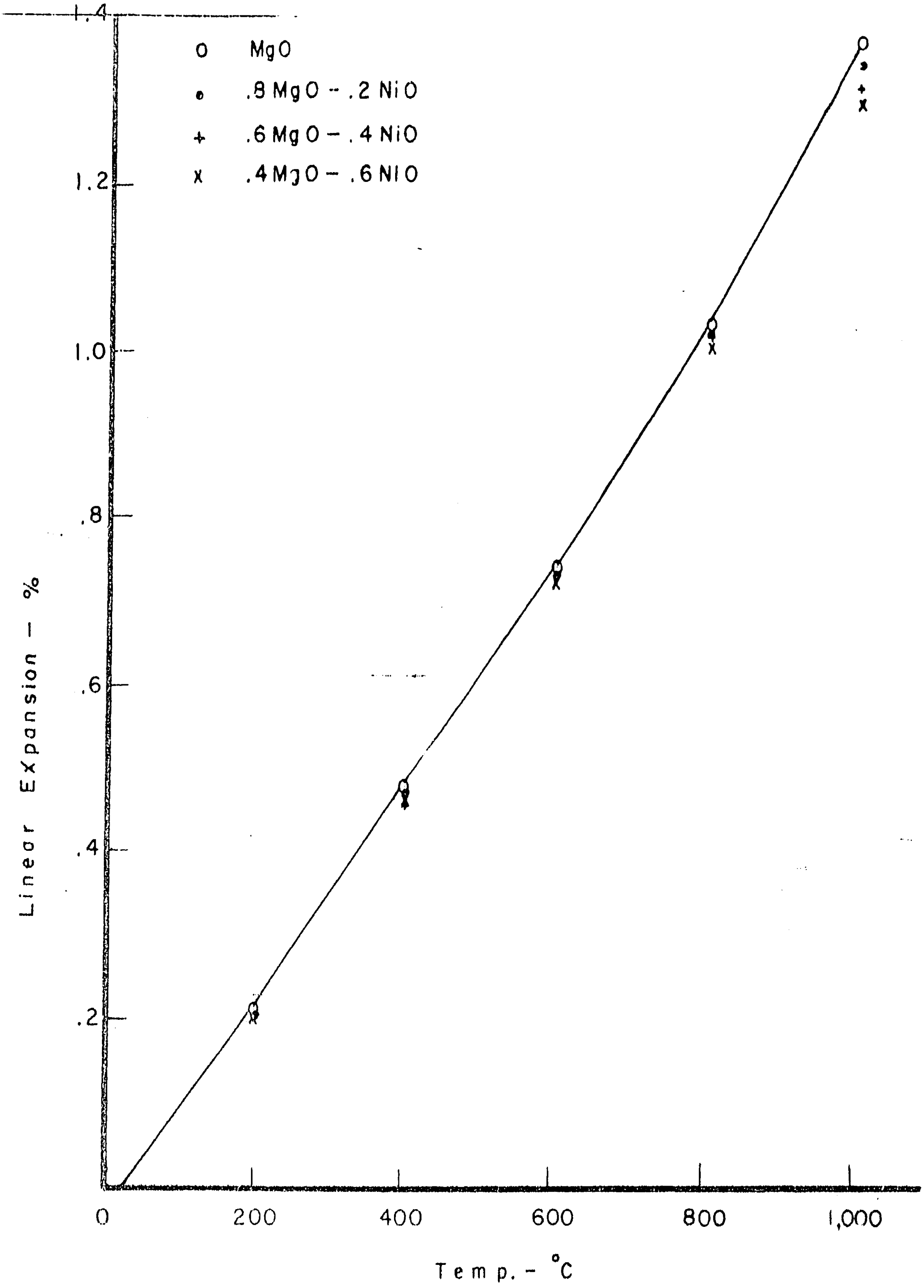


FIGURE I. THERMAL EXPANSION OF MgO-NiO SOLID SOLUTIONS

TABLE IV

Thermal Expansion Data for MgO-NiO Solid Solutions

	Pure MgO				0.8 MgO-0.2 NiO			
Temp.	Angle	d	Δ d	% Exp.	Angle	d	Δ d	% Exp.
Rm. T	127.245	.85976	---	---	127.64	.85830	---	---
200	126.770	.86154	.00178	0.207	127.18	.86000	.00170	0.199
400	126.160	.86386	.00410	0.477	126.575	.86228	.00398	0.464
600	125.575	.86612	.00636	0.740	125.98	.86455	.00625	0.729
800	124.915	.86870	.00894	1.030	125.33	.86707	.00877	1.022
1000	124.230	.87143	.01167	1.358	124.645	.86977	.01147	1.337
	0.6 MgO-0.4 NiO				0.4 MgO-0.6 NiO			
Rm. T	128.185	.85631	---	---	128.485	.85522	---	---
200	127.72	.85801	.00170	0.199	128.00	.85698	.00176	0.206
400	127.115	.86024	.00393	0.449	127.385	.85925	.00403	0.471
600	126.49	.86260	.00629	0.734	126.790	.86147	.00625	0.730
800	125.865	.86499	.00868	1.020	126.185	.86376	.00854	1.001
1000	125.23	.86746	.01115	1.303	125.530	.86629	.01107	1.295

When a more reactive material containing MgO, for example $MgCO_3$, is used as the starting material the resulting product contains spinel plus a small amount of corundum (Al_2O_3). The 0.3 MgO-0.7 Al_2O_3 composition contains spinel plus a minor amount of corundum. The lattice spacings of the spinel are shifted to smaller values, apparently by solution of aluminum oxide in the spinel lattice.

The thermal expansion curves for the alumina-rich spinel and the more stoichiometric spinel are shown in Figure 2. The data are given in Table V. The thermal expansion coefficients of the alumina-rich spinel are substantially lower than the thermal expansion coefficients of the more stoichiometric material. Although the compositions of the solutions measured in these cases are not known, sufficient thermal expansion difference was observed to give rise to stresses that are large enough to justify further consideration of these materials for formation of compressive surface layers.

Thermal Expansion of Other Solid Solutions

Al_2O_3-Ga_2O_3 System

The X-ray pattern of the sample of the composition 0.8 Al_2O_3-0.2 Ga_2O_3 indicated a mixture of α Al_2O_3 and β Ga_2O_3 with substantial shifting of the Al_2O_3 peaks due to solution of Ga_2O_3 in the Al_2O_3. Although the composition of the solid solution is not known, a preliminary thermal expansion measurement was made to get some indication of the results to be

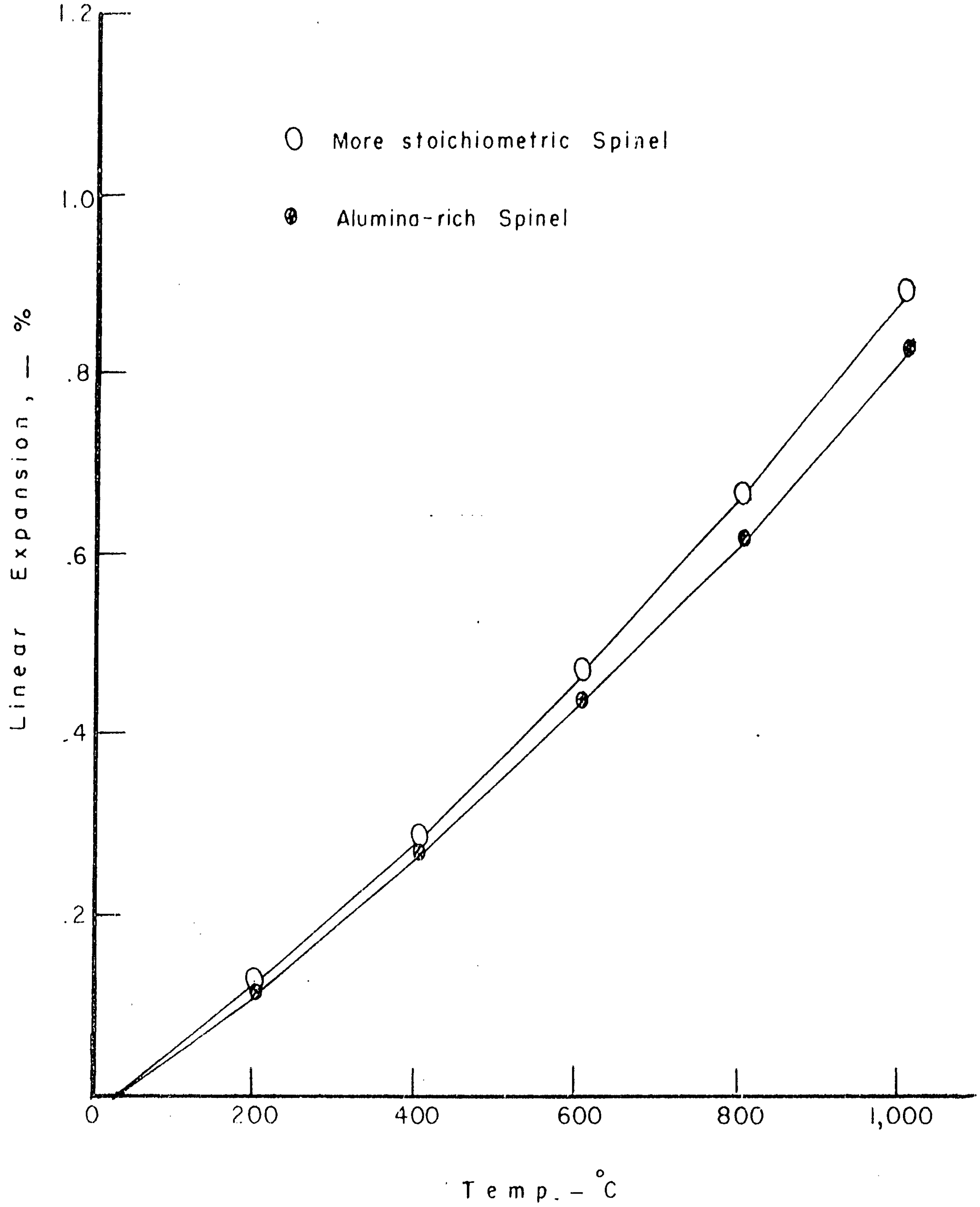


FIGURE 2. THERMAL EXPANSION OF AN ALUMINA-RICH SPINEL COMPARED WITH A MORE STOICHIOMETRIC SPINEL

TABLE V

Thermal Expansion of Alumina-Rich Spinel (From reaction of composition 0.3 MgO-0.7 Al_2O_3)

Temp.	Angle	d	Δ d	% exp.
27.5°C	141.03	.81704	---	---
200	140.66	.81798	.00094	0.115
400	140.175	.81922	.00218	0.267
600	139.64	.82063	.00359	0.439
800	139.08	.82211	.00507	0.621
1000	138.455	.82380	.00676	0.828

TABLE VI

Thermal Expansion of More Stoichiometric Spinel (From reaction of composition 0.5 MgO-0.5 Al_2O_3)

Temp.	Angle	d	Δ d	% exp.
26.5	137.98	.82510	---	---
200	137.62	.82611	.00101	0.122
400	137.13	.82749	.00239	0.290
600	136.61	.82897	.00387	0.469
800	136.04	.83062	.00552	0.669
1000	135.44	.83240	.00730	0.896

expected in this system. The solid solution has slightly larger thermal expansion coefficients and slightly larger thermal expansion anisotropy than the pure aluminum oxide.

Al_2O_3-Cr_2O_3 System

The X-ray diffraction patterns of several solid solution compositions in this system showed complete reaction to form a single phase but the solid solutions formed were inhomogeneous so that the diffraction peaks in the back-reflection region were very broad. Thermal expansion measurements using the broad back-reflection peaks and the sharper peaks at smaller diffraction angles led to unreliable results. In order to form more homogeneous solutions, it is planned to coprecipitate the two oxides from water solution so that the materials will be very intimately mixed before firing.

TiO_2-SnO_2-VO_2 System

Before beginning work on this present program it was known that TiO_2-SnO_2 solid solutions had lower thermal expansion coefficients than the pure TiO_2 and that TiO_2-VO_2 and SnO_2-VO_2 solid solutions had lower thermal expansion anisotropy than the pure TiO_2. Therefore, it seems reasonable to expect that relatively low-expansion surface layers with reduced thermal expansion anisotropy can be found in the TiO_2-SnO_2-VO_2 system. Preliminary X-ray diffraction measurements indicate that firing temperatures high enough to react the TiO_2 and SnO_2 result in loss of the VO_2 by evaporation. It is planned to react the TiO_2 and SnO_2 in advance and then add the VO_2 to the TiO_2-SnO_2 solution to attempt to prepare solutions of the desired composition.

MgO-ZnO System

X-ray diffraction examination of fired mixtures in the MgO-ZnO system indicated no change in the lattice constants of the MgO and substantial remaining ZnO, for the firing treatments used. Low intensity peaks indicated the presence of an unidentified phase. No further experiments are planned with this system.

B. Formation of Compressive Surface Layers

When it was found that a solid solution of tin oxide in rutile had a coefficient of thermal expansion less than that of rutile (see Table I), a chemical approach to producing compressive surface layers in oxide polycrystalline ceramics was available for study. The relatively low firing temperature of titania together with its extensive solid solution with tin oxide make it a good choice for preliminary studies of the feasibility of the proposed strengthening method. Disadvantages of the titania-tin oxide system are the low tensile strength of rutile bodies (as compared to alumina bodies) and the refractoriness of tin oxide.

The concentration of the tin oxide in this surface layer solid solution should decrease from the surface to the interface zone in order to reduce the tendency for the compression layer to shear from the interface with the titania body.

A rational basis for determining the optimum thickness of the compressive surface layers is not available at the present time. It is clear, though, that the compressive surface layers should be thicker than the expected flaws due to abrasion. In the case of artifically abraded glasses with compressive surface layers, a compressive layer thickness of more than 80 μ was reported necessary by Nordberg et al$^{(6)}$ to retain modulus of rupture values above 50,000 psi. On the other hand, the compressive surface layers should not be so thick that they significantly increase the tensile stresses in the core.

Sample Preparation

The specimens were prepared from TAM heavy grade titanium oxide.

Sieve Analysis % = 0.1% max. + 325 mesh
Particle Size = 0.5 to -3.0 microns
TiO_2 = 98.0 - 99.0%
SiO_2 = 0.4 - 0.8%
Al_2O_3 = 0.5% max.
Ignition Loss = 0.25% max.

Tin was added to the titania as C.P. stannic oxide, stannous chloride, or stannic chloride.

The first samples, pressed from dry powder, were too difficult to handle and polyvinyl alcohol (Evanol 51-05) was added to the dry powder as a binder.

Two and one-half to five per cent (by weight) of the (15 gram of Evanol in 85 ml water) binder solution was added to the dry powder and mixed in a mortar and pestle. Bars (3" by 3/8" by 1/4") were pressed in a steel mold at various pressures. Good samples were obtained at pressures of 5,000 to 10,000 pounds per square inch. At higher pressures, 15,000, 20,000 and 25,000 psi, the body showed laminations. In this method (wet binder) of adding the binder, there seems to be an excess of water in the pressed specimen as it is taken from the mold. A second method (dry binder) of adding the binder to the mix was used in order to produce a dryer bar. Nine per cent of a (25 gram Evanol to 75 ml water) binder solution was added to the powder, thoroughly mixed, and then dried at 110°C overnight. The dried binder and powder is then broken up in a mortar and pestle, 0.75 per cent water is added and again well mixed. This mixture is pressed at 20,000 and 25,000 psi in the steel mold. All bar samplesweighed approximately twelve grams.

All firing of the samples was done in an electrically heated furnace and temperatures were read with a platinum-platinum 10% rhodium thermocouple.

Formation of Solid Solution Surface Layers

The following methods were used to introduce tin into the unfired titania bars:

1. dipping
2. painting

Dipping into solutions of tin compounds in water or alcohol resulted in disintegration of the unfired bars so this method was abandoned. Painting resulted in apparently uniform layers and avoids the disintegration.

A dye, eosin (0.05 gms in 1 ml. alcohol), was added to the tin solutions in some cases to determine the depth of penetration. Sample bars pressed at 5000 psi could be stained to a depth of two millimeters with the pink dye.

Control of Porosity Before Firing

1. Wet binder method - Bars made by this method seemed to be least porous and the tin solutions containing dye remained on the surface.

2. Dry binder method - Bars made by this method seemed to have good porosity and the tin solutions had good penetration into the unfired titania bar.

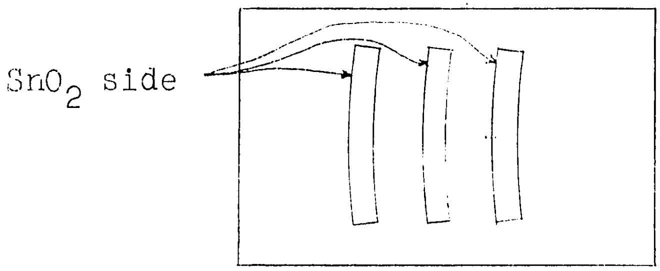
3. Burn-out of organic materials - Titania bars were made porous by burn-out of organic materials; for example, powdered rosin or sugar to give the following results:

Material	Firing Temp.	Apparent Porosity	Density
TiO_2	1000°C 1 hr.	34.0	2.42
TiO_2 + 10% Rosin	1000°C 1 hr.	40.9	2.08
TiO_2	1500°C 1 hr.	.3*	4.04

* Low apparent porosity may be due to sealed pores.

Bars made with rosin or sugar were very much alike and had a good appearance.

Unfired titania bars (3" by 1/3" x 1/4") were covered with a tin solution (one gram $SnCl_4 \cdot 5\ H_2$) on the widest face (3" x 1/3"). They were then fired to 1500°C for one hour resting on the narrowest face (3" by 1/4") on a zirconia plate. The sample bar bent as shown below:



This bending might be caused by sintering of the titania body at a lower temperature than the tin oxide side of the bar, by the fact that there is more material present on the coated side, or by residual stresses. A bar coated with tin solution in the same manner as above but on both sides, remains straight and does not bend. A slice, approximately two millimeters thick and containing one tin oxide-titania solid solution face and one titania face, was cut from this bar. No detectable bending, due to residual stresses, was noted. The cause of this bending remains uncertain.

Attempts to increase the sintering of the SnO_2 layer by the addition of CuO to the SnO_2 were made, since it was found, as shown in Table VII, that 0.5 mole per cent CuO in tin oxide would produce a sintering shrinkage almost as great as that found in titania alone at the same temperature. However, when a titania bar containing tin oxide and copper oxide was fired as shown in Table VII, the sintering shrinkage was reduced to 12-13 per cent.

Table VII contains data indicating that bars of 20 mole per cent SnO_2 in titania, and titania, have approximately the same sintering shrinkage characteristics in the temperature range 1400° to 1500°C.

Chemical Composition of Surface Layers

In order to understand the stress gradient in bodies with compressive surface layers, it is necessary to know the relationship between composition and thermal expansion, and the composition variations in the body. Of the several methods that could be used to determine the compositions at various positions in the treated bodies, the most convenient method for use in this program makes use of the variation of the lattice constants with tin additions to form solid solutions. Standard solid solution samples of known composition were prepared and the variation of diffraction angle and with composition were determined for two diffraction peaks. The composition of unknowns is determined by determining the peak position and reading the composition from the standard curve.

TABLE VII

Comparison of Per Cent Linear Shrinkage vs. Heat Treatment for TiO_2 - SnO_2 Bars

Composition of Bar	1400°C		1450°C	1500°C
	1 hr.	8 hrs.	4 hrs.	1 hr.
TiO_2 Wet Mix 10,000 psi	--	15.1	15.0	15.9
TiO_2 Dry Mix 25,000 psi	15.2	--	--	--
80 TiO_2:20 SnO_2	15.5	--	--	15.8
80 TiO_2:19.5 SnO_2: 0.5 CuO	--	12.2	12.7	12.0
99.5 SnO_2:0.5 CuO added as CuO	--	14.7	15.6	14.6
99.5 SnO_2:0.5 CuO added as $CuSO_4$:5 H_2O	--	13.8	16.2	15.6
SnO_2	--	8.2	4.9	2.9

This method was applied to several unknowns. Useful results were obtained. In one case 7.5% SnO_2 was found in solution in the surface of a treated sample. This tin oxide content is sufficient to introduce significant stresses.

Determination of Grain Size

Thin sections were cut and ground from titania samples fired to (1) 1500°C for one hour, (2) 1450°C for one hour, and (3) from a 80% TiO_2-20% (mole) SnO_2 sample fired to 1500°C for one hour. The thin section of the titania sample fired to 1500°C appears to be slightly more transparent and contains slightly larger crystals (10 to 18 microns) than the section of the bar fired to 1450°C (8 to 15 microns). Very little difference could be found between the section of the 80% TiO_2:20% SnO_2 sample compared with the titania sections.

A polished section, etched with potassium bisulfate showed a slight tendency for the individual crystal grains to stand out in relief but, on the whole, the surface was rapidly and uniformly etched back as a smooth surface.

Variation of Strength with Firing Temperature

A preliminary series of firings was made as reported in Table VIII to determine the effect of peak temperature and time on the modulus of rupture of titania bars. Modulus of rupture was measured by three-point loading over a two-inch span applying the load at 10,000 psi per minute.

TABLE VIII

Modulus of Rupture vs. Firing Conditions

Sample No.	Wt.	Press	Firing Time	Temp.	Modulus of Rupture in psi
#1	12	10,000	1 hr	1,400°C	13,000
#2	12	10,000	1 hr	1,100°C	17,200
			1 hr	1,100°C	
			1 hr	1,400°C	
#3	12	10,000	1 hr	1,500°C	10,680
#4	12	10,000	1 hr	1,500°C	10,128
#5	12	10,000	1 hr	1,500°C	10,000
#6	12 gm (Dry Mix)	24,000	1 hr	1,380°C	16,551

The data from this series of firings indicates that a short (one hour at peak temperature) firing at 1500°C on a bar pressed at 10,000 psi produces a relatively weaker body than a similar firing time at 1400°C.

The bar that had a longer soak period at 1100°C with a final peak temperature of 1400°C has a higher strength than the 1400°C bar with no soak period. Pressing a bar at 25,000 psi and firing at 1400°C results in a strength comparable with that of the bar pressed at a lower pressure with a longer firing time.

III. CONCLUSIONS

A. Periclase solid solutions in the system MgO-NiO have thermal expansion coefficients that are lower than the thermal expansion coefficients of the relatively pure MgO on which they might be used to form compressive surface layers.

B. Spinel solid solutions in the system $MgO \cdot Al_2O_3$-Al_2O_3 have thermal expansion coefficients that are lower than the thermal expansion coefficients of the relatively pure $MgO \cdot Al_2O_3$ on which they might be used to form compressive surface layers.

C. Addition of solid solutions in the above systems to the list of available low-expansion solid solutions has substantially increased the chances of success in this research program by increasing the number of material combinations that can be investigated as surface and base materials.

D. TiO_2-SnO_2 solid solution layers can be formed on the surface of TiO_2 bodies.

IV. PLANS FOR THE NEXT PERIOD

A. Thermal Expansion Research

The search for additional solid solutions having lower thermal expansion coefficients than a pure component will be continued. This work will include investigations of systems not previously investigated, attempts to obtain more homogeneous solid solutions in the systems Al_2O_3-Cr_2O_3 and TiO_2-SnO_2-VO_2, and attempts to obtain more complete reaction between Al_2O_3 and Ga_2O_3.

B. Preparation of Compressive Surface Layers

Preparation of TiO_2-SnO_2 solid solution surface layers on TiO_2 bodies will be continued. In addition, a second system will be selected for investigation and compressive surface layers will be prepared using compositions in this system.

C. Investigation of Stresses in Compressive Surface Layers

Preliminary investigations of the stresses in compressive surface layers will be conducted. The X-ray diffraction method and the change in curvature when part of a stressed body is removed will be used as methods of measurement. Analytical methods of stress determination will be investigated.

V. REFERENCES

1. R. H. Stutzman, J. R. Salvaggi and H. P. Kirchner, "The Thermal Expansion of Ceramic Materials, Vol. I, Literature Survey" Cornell Aeronautical Laboratory Report No. PI-1273-M-4, Contract No. NOrd-18419 (August 31, 1959).

2. H. P. Kirchner, "The Thermal Expansion of Ceramic Crystals" from "Progress in Solid State Chemistry" Pergamon Press, New York (1964).

3. H. P. Kirchner, H. A. Scheetz, W. R. Brown and H. T. Smyth, "The Thermal Expansion of Ceramic Materials" Cornell Aeronautical Laboratory Report No. PI-1273-M-12, Contract No. NOrd-18419 (July, 1962).

4. K. M. Merz, W. R. Brown and H. P. Kirchner, "The Thermal Expansion Anisotropy of Oxide Solid Solutions" J. Am. Ceram. Soc. 45 (11) 531 (1962).

5. J. G. Stradley et al., "Stresses in Polycomponent Solid Ceramics or Cermets," Ohio State University Res. Found. Rep. No. 806-1, Contract AF33(616)-5515 (July, 1958).

6. M. E. Nordberg et al., "Strengthening by Ion Exchange" J. Am. Ceram. Soc. 47(5)215 (May, 1964).

DISTRIBUTION LIST

				No. of Copies
1.	Bureau of Naval Weapons, Washington, D. C. 20360, Attn: DLI-31			28
	For distribution as follows:	RRMA-31	5	
		RRMA-23	1	
		DLI-31	2	
		DLI-302(DDC)	20	
2.	Air Force Materials Laboratory, Research and Technology Division AFSC, Wright-Patterson Air Force Base, Ohio 45433			
	Attn:	MAMC		1
		MAAE		1
		MAAM		1
3.	Defense Metals Information Center, Battelle Memorial Institute, 505 King Avenue, Columbus, Ohio 43201			1
4.	Illinois Institute of Technology Research Institute, 10 West 35th Street, Chicago, Illinois 60616			
	Attn:	Metals and Ceramics Division		1
		Mechanics Research Division		1
5.	Department of Metallurgy, Massachusetts Institute of Technology, Cambridge, Massachusetts			1
6.	Pittsburgh Plate Glass Company, Glass Research Center, Box 11472 Pittsburgh, Pennsylvania 15238			1
7.	Materials Research Corporation, Orangeburg, New York 10962			1
8.	Atomics International Division, North American Aviation, Inc., P. O. Box 309, Canoga Park, California			1
9.	Minneapolis-Honeywell Regulator Company, Research Center, Hopkins, Minnesota			1
10.	Boeing Airplane Company, Aerospace Division, P. O. Box 3707, Seattle 24, Washington			1
11.	School of Ceramics, Rutgers, The State University, New Brunswick, New Jersey			1

DISTRIBUTION LIST (Cont.)

		No. of Copies
12.	State University of New York, College of Ceramics at Alfred University, Alfred, New York	1
13.	Corning Glass Works, Corning, New York	1
14.	Georgia Institute of Technology, Engineering Experiment Station, Atlanta, Georgia 30332	1
15.	Hughes Aircraft Company, Florence and Teale Streets, Culver City, California Attn: L. E. Gates, Mail Station X122	1
16.	Atomic Energy Commission, Technical Information Service, P. O. Box 62, Oak Ridge, Tennessee	1
17.	Materials Sciences Laboratory, United Aircraft Corp., East Hartford 8, Connecticut	1
18.	Narmco R & D, 3540 Aero Court, San Diego, California 92123	1
19.	Avco Corporation, 201 Lowell Street, Wilmington, Massachusetts Attn: Metals and Ceramics Division	1
20.	Southern Research Institute, Inorganic Materials Section, 2000 9th Avenue, S., Birmingham 5, Alabama	1